Synthesis and characterization of mesostructured aluminophosphates using the fluoride route

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The room-temperature synthesis of the hexagonal mesostructured aluminophosphate and its phase transition into the lamellar phase are reported.

Since Mobil researchers first demonstrated in 1992 that through a micelle-assisted crystallization of the inorganic phase, the hexagonally packed mesoporous silicate and aluminosilicate materials (MCM-41) with uniformly sized pores could be synthesized,[1] there has been much interest in synthesizing mesoporous aluminophosphates owing to the previous success in the synthesis of microporous aluminophosphates[2] with framework topology identical or similar to aluminosilicate zeolites. However, so far attempts in synthesizing the mesostructured aluminophosphates have had very limited success.

It has been demonstrated that lamellar aluminophosphates can be made from non-aqueous or aqueous systems by using a liquid-crystal templating approach.[3–7] The presence of the hexagonal mesostructured aluminophosphate has been suggested in a brief description by Kimura *et al.*[8] Here, we demonstrate that in the presence of F^- ions and using EtOH–H_2O as a solvent, pure hexagonal mesostructured aluminophosphate of relatively high quality can be obtained. We have found that the formation of the hexagonal phase precedes the formation of the lamellar phase and that a phase transition from the hexagonal phase to the lamellar phase in the aluminophosphate system can be induced.

A typical sample preparation was: aluminium isopropoxide (4.01 g) was mixed with 7.28 g of ethanol. After stirring, 40.0 g of distilled water was added, followed by the addition of 2.79 g of 85% H_3PO_4 and 0.67 g of 49% HF. After further stirring, 1.86 g of $C_{16}H_{33}Me_3NBr$ (surfactant/Al ratio = 0.26) was added. Finally, 10.40 g of 25% NMe_4OH was slowly added until the pH of the solution was *ca.* 8.3. The mixture was stirred at room temp. for 4 h. The pure hexagonal mesostructured phase was obtained after filtering and washing with distilled water. However, if after stirring for 4 h at room temp. the gel was placed in an oven at 70 °C for a few days, the hexagonal phase was converted partially into a mesostructured lamellar phase. At higher temperatures such as 100 °C, the transition to the lamellar phase proceeded at a faster rate and the complete conversion took only 2 days. The X-ray powder patterns with different reaction conditions are shown in Fig. 1.

Postsynthesis treatment was found to enhance the crystalline quality of the hexagonal mesostructured phase.[9] The above-room-temperature synthesized hexagonal sample was further treated by putting the sample into deionized water at 70 °C for about a week, then filtered and dried. The sample was subsequently stirred in ethanol overnight, filtered off and dried. The intensity of the XRD peaks was greatly enhanced by this treatment. The treated sample was used for the subsequent characterization including TEM and ^{27}Al MAS NMR.

The hexagonal phase obtained was further confirmed by the TEM image (Fig. 2) which was recorded on a 2000FX JEOL microscope operated at 200 keV. The TEM sample was prepared by collecting a large number of crystallites onto a holey carbon film on a Ni grid. ^{27}Al MAS NMR spectra were obtained on a General Electric GN-300 spectrometer system at a frequency of 78.30 MHz with a spinning speed of *ca.* 5 kHz, a delay time of 2 s. and a pulse width of 4.0 μs. A four-pulse composite 90° pulse was used for background suppression.[10] Aluminium nitrate solution was used as external reference. The ^{27}Al MAS NMR of the hexagonal mesostructured material gave two lines at δ 43.8 and -8.7 corresponding to tetrahedrally and octahedrally coordinated Al species, respectively. ^{27}Al NMR of

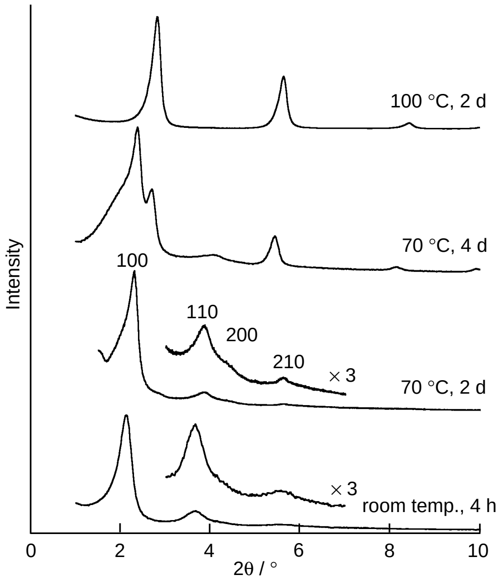

Fig. 1 Powder diffraction patterns showing the phase transition from the hexagonal phase to the lamellar phase under different reaction conditions

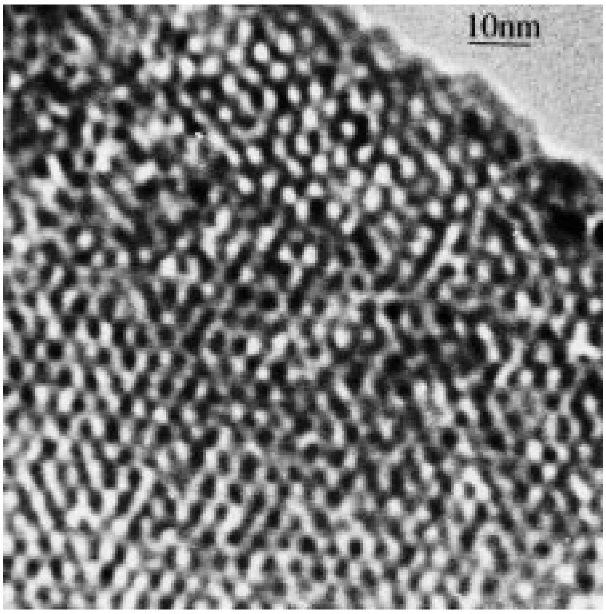

Fig. 2 The TEM image of the hexagonal mesostructured aluminophosphate

the lamellar mesostructure showed one narrow line at δ 40.06 and a very small bump at δ −8.2 suggesting the tetrahedral coordination for the majority of the Al species in the lamellar phase (Fig. 3). The inclusion of F^- anions into the hexagonal phase was verified by elemental analysis (results in mass%: 9.38 Al, 9.14 P, 3.56 F, 26.19 C, 1.55 N, 7.77 H, <0.5 Br) which was performed by Galbraith Laboratories, Inc. The molar ratio between polyhedral centres (Al + P) and the surfactant is comparable to that found in the silica-based MCM-41 material.[11] Thermogravimetric analysis (TG) and differential thermal analysis (DTA) on the hexagonal phase showed that the mass loss occurred between 300 and 700 °C accompanied by endothermic events. The calcination of the as-synthesized hexagonal phase into a mesoporous structure has not yet been achieved and further investigation is in progress.

Compared to silica-based mesoporous materials, the formation of aluminophosphate mesostructured phases appears more sensitive to some of the starting materials. For example, both NaOH and NMe_4OH have been successfully used in the synthesis of silica-based mesoporous materials. However, when NaOH, KOH or NH_4OH were used as the base in place of NMe_4OH in the phosphate system, only amorphous materials were obtained. The source of aluminium is another important factor. In our experiments, the use of either $Al(NO_3)_3$ or Catapal B alumina as the aluminium source also led to amorphous materials. However, the surfactant/Al ratio could be varied within a certain range since we found that the same hexagonal phase could be prepared with a surfactant/Al ratio of 0.90. The use of ethanol as the cosolvent together with the addition of HF is necessary in order to synthesize good quality materials.

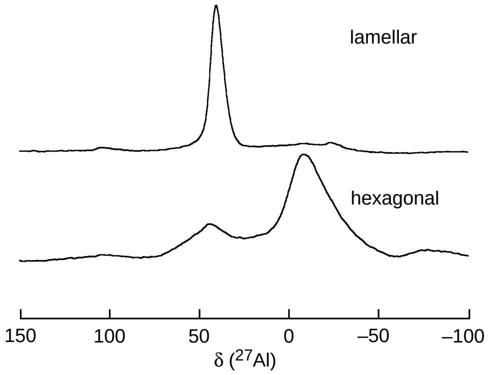

Fig. 3 ^{27}Al NMR spectra showing that the hexagonal–lamellar phase transition is accompanied by a change in the Al coordination polyhedra

It is of interest to compare the relative stability of hexagonal and lamellar phases in the aluminophosphate system with those in the silica-based phases. Both lamellar–hexagonal and hexagonal–lamellar phase transitions have been reported for the silica-based materials prepared using $NMe_3(C_{16}H_{33})^+$ and $NMe_3(C_{20}H_{41})^+$.[9,11,12] In the aluminophosphate system, we find that the hexagonally packed aluminophosphate undergoes a phase transition into the lamellar phase under hydrothermal treatment similar to that employed for the silica-based material.[9] Noteworthy in this regard is the tetrahedral coordination of the Al in the lamellar phase, suggesting that condensation of the octahedral aluminium species found in the hexagonal phase is an important factor in the phase transformation of this mesostructured aluminium phosphate.

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